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Title: A Novel Platform for Studying Hot Electron Spectroscopy of Electrochemical and Photoelectrochemical Reactions

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Progress: During the funding period, six papers were published with support from the ACS PRF.

Hot electron-driven photocatalytic water splitting¹

During this funding period, we reported measurements of photocatalytic water splitting using Au films with and without TiO₂ coatings. In these structures, a thin (3-10nm) film of TiO₂ is deposited using atomic layer deposition (ALD) on top of a 100nm thick Au film. We utilize an AC lock-in technique, which enables us to detect the relatively small photocurrents (~μA) produced by the short-lived hot electrons that are photoexcited in the metal. Under illumination, the bare Au film produces a small AC photocurrent (<1 μA) for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) due to hot electrons and hot holes, respectively, that are photoexcited in the Au film. The samples with TiO₂ produce a larger AC photocurrent indicating that hot electrons are being injected from the metal into the TiO₂ semiconductor where they then reduce hydrogen ions in solution forming H₂ (i.e., $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). The AC photocurrent exhibits a narrow peak when plotted as a function of reference potential, which is a signature of hot electrons. Here, we photoexcite a monoenergetic source of hot electrons, which produces a peak in the photocurrent, as the electrode potential is swept through the resonance with the redox potential of the desired half-reaction. This stands in contrast to conventional bulk semiconductor photocatalysts, whose AC photocurrent saturates beyond a certain potential (i.e., light limited photocurrent). The photocurrents produced at the metal-liquid interface are smaller than those of the metal-semiconductor system, mainly because, in the metal-semiconductor system, there is a continuum of energy and momentum states that each hot electron can be injected into, while for an ion in solution, the number of energy and momentum states are very small.

Prevention of surface recombination by electrochemical tuning of TiO₂-passivated photocatalysts²

We also presented a systematic study of photoluminescence (PL) spectroscopy of TiO₂-passivated GaAs as a function of electrochemical potential in an ionic liquid solution. We observe a 7X increase in the PL intensity as the GaAs transitions from accumulation to depletion due to the applied potential. We attribute this to the excellent control over the surface Fermi level enabled by the high capacitance of the electrochemical double layer and TiO₂. This allows us to control the surface carrier concentration and corresponding non-radiative recombination rate. In addition to photoluminescence (PL) spectroscopy, we also measured the capacitance-potential (i.e., C-V) characteristics of these samples, which indicate flat band potentials that are consistent with these regimes of ion accumulation observed in the photoluminescence measurements. We have also performed electrostatic simulations of these C-V characteristics, which provide a detailed and quantitative picture of the conduction and valence band profiles and charge distribution at the surface of the semiconductor. These simulations also enable us to determine the range of potentials over which the semiconductor surface experiences depletion, inversion, and accumulation of free carriers. Based on these simulations, we can calculate the Shockley-Read-Hall recombination rate and model the PL intensity as a function of voltage. We show that this approach allows us to explain our experimental data well.

Plasmon resonant amplification of a hot electron-driven photodiode³

We report plasmon resonant excitation of hot electrons in a photodetector based on a metal/oxide/metal (Au/Al₂O₃/graphene) heterostructure. In this device, hot electrons, excited optically in the gold layer, jump over the oxide barrier and are injected into the graphene layer, producing a photocurrent. To amplify this process, the bottom gold electrode is patterned into a plasmon resonant grating structure with a pitch of 500 nm. The photocurrent produced in this device is measured using 633-nm-wavelength light as a function of incident angle. We observe the maximum photocurrent at ±10° from normal incidence under irradiation with light polarized parallel to the incident plane (p-polarization) and perpendicular to the lines on the grating, and a constant (angle-independent) photocurrent under irradiation with light polarized perpendicular to the incident plane (s-polarization) and parallel to the grating. These data show an amplification factor of 4.6× under resonant conditions. At the same angle (±10°), we also observe sharp dips in the photoreflectance corresponding to wavevector matching between the incident light and the plasmon mode in the grating. In addition, finite-difference time-domain simulations predict sharp dips in the photoreflectance at ±10°, and the electric field intensity profiles show clear excitation of a plasmon resonant mode when illuminated with p-polarized light at this angle.

Sensing local pH and ion concentration at graphene electrode surfaces using *in situ* Raman spectroscopy⁴

We report a novel approach to probe the local ion concentration at graphene/water interfaces using *in situ* Raman spectroscopy. Here, the upshifts observed in the G band Raman mode under applied electrochemical potentials are used to determine the charge density in the graphene sheet. For voltages up to ± 0.8 V vs. NHE, we observe substantial upshifts in the G band Raman mode by as much as 19 cm^{-1} , which corresponds to electron and hole carrier densities of $1.4 \times 10^{13}\text{ cm}^{-2}$ and Fermi energy shifts of ± 430 meV. The charge density in the graphene electrode is also measured independently using the capacitance–voltage characteristics (i.e., $Q = CV$), and is found to be consistent with those measured by Raman spectroscopy. From charge neutrality requirements, the ion concentration in solution per unit area must be equal and opposite to the charge density in the graphene electrode. Based on these charge densities, we estimate the local ion concentration as a function of electrochemical potential in both pure DI water and 1 M KCl solutions, which span a pH range from 3.8 to 10.4 for pure DI water and net ion concentrations of $\pm 0.7\text{ mol L}^{-1}$ for KCl under these applied voltages.

Plasmon resonant amplification of hot electron-driven photocatalysis⁵

We report plasmon resonant excitation of hot electrons in a metal based photocatalyst in the oxygen evolution half reaction in aqueous solution. Here, the photocatalyst consists of a 100-nm thick Au film deposited on a corrugated silicon substrate. In this configuration, hot electrons photoexcited in the metal are injected into the solution, ultimately reversing the water oxidation reaction ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$) and producing a photocurrent. In order to amplify this process, the gold electrode is patterned into a plasmon resonant grating structure with a pitch of 500 nm. The photocurrent (i.e., charge transfer rate) is measured as a function of incident angle using 633 nm wavelength light. We observe peaks in the photocurrent at incident angles of $\pm 9^\circ$ from normal when the light is polarized parallel to the incident plane (p-polarization) and perpendicular to the lines on the grating. Based on these peaks, we estimate an overall plasmonic gain (or amplification) factor of $2.1\times$ in the charge transfer rate. At these same angles, we also observe sharp dips in the photoreflectance, corresponding to the condition when there is wavevector matching between the incident light and the plasmon mode in the grating. No angle dependence is observed in the photocurrent or photoreflectance when the incident light is polarized perpendicular to the incident plane (s-polarization) and parallel to the lines on the grating. Finite difference time domain simulations also predict sharp dips in the photoreflectance at $\pm 9^\circ$, and the electric field intensity profiles show clear excitation of a plasmon-resonant mode when illuminated at those angles with p-polarized light.

Impact: The research performed under this award has impacted the PIs' careers by enabling them to pursue a new research direction that would otherwise not have been possible without these funds. Several publications resulted from this work, which positively impacts the careers of the PIs and their students supported under this grant.

References

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